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Soluble Phenyl- or Alkoxyphenyl-Substituted Rigid-Rod Polyamides and Polyimides Containing *m*-Terphenyls in the Main Chain

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ABSTRACT: 4,4′′-Diamino-5′-phenyl- or 4-alkoxyphenyl-*m*-terphenyl and 4,4′′-dicarboxy-5′-phenyl-*m*-terphenyl were synthesized through pyrylium salts and used for the preparation of rigid-rod polyamides and polyimides. The polymers were characterized by inherent viscosity, elemental analysis, FT-IR, UV−vis, ^{1}H NMR, ^{13}C NMR, X-ray, DSC, TMA, TGA, isothermal gravimetric analysis, and moisture absorption. It was shown that the presence of the 4-alkoxyphenyl pendent groups enhanced remarkably the solubility of polymers as well as reduced the T_g's and thermal stability. In addition, the polyamide bearing 4-(dodecyloxy)phenyl side groups displayed softening.

Introduction

Aromatic rigid-rod polyamides and polyimides constantly attract much interest because of their unique mechanical,[1] optical, and morphological[2,3] properties. However, these materials present often poor processability due to their limited solubility and infusibility. Attachment of aromatic or aliphatic pendent groups along the polymer backbone was found to be an effective approach to increase their solubility and reduce the transition temperatures. Aromatic substituents have been used extensively to prepare soluble rigid-rod polyamides[4−13] and polyimides.[14−18] The use of long alkyl groups as lateral substituents has also led to an increase of solubility, remarkably lower melting and glass transition temperatures, and unique layered crystal stucture.[19−24] It is interesting that unsubstituted poly(1,4-phenyleneterephthalamide) exhibits a lyotropic mesophase, while appending flexible side groups leads to thermotropic behavior.[25] However aliphatic substituents reduce the thermal stability of the polymers.

Another approach employed to increase the solubility of rigid-rod polyamides and polyimides is the incorporation of nonlinear moieties in the main chain.[26,27] Previous works[28,29] showed that polyamides containing unsubstituted *p*-terphenyls in the main chain were completely insoluble even in strong acids. Replacing *p*-terphenyls with the nonlinear *o*-terphenyls resulted in polymers soluble in polar aprotic solvents, without considerable influence on their thermal stability.[30]

The present work is a continuation of our research on preparing soluble rodlike polyamides and polyimides. In previous works[31−34] we described the synthesis of soluble polyamides and polyimides by introducing aromatic pendent groups along the polymer backbone. The side groups twist the oligophenylene moieties of the main chain out of a planar conformation, thereby increasing solubility. In this article we report the synthesis and characterization of soluble rigid-rod polyamides and polyimides containing *m*-terphenyl units in the main chain. The introduction of *m*-terphenyl into the polymer chain reduces the symmetry and improves the solubility. In addition, pendent phenyl or alkoxyphenyl groups have been incorporated in order to contribute to the increase of solubility. *m*-Terphenyl segments have also been used in luminescent polyphenylenes to interrupt the conjugation and to control the emitter units.[35]

Experimental Section

Characterization Methods. Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV/vis spectra were recorded on a Beckman DU-640 spectrometer with spectograde DMF. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA and isothermal gravimetric analysis (IGA), and the weight loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20 °C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted in duplicate. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powdered polymer for 3 min under 5−7 kpsi at ambient temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in H_2SO_4 or DMAc at 30 °C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, polymer samples were previously conditioned at 120 °C in an oven for 12 h. They were subsequently placed in a desiccator where 65% rh (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20 °C and were periodically weighed.

Reagents and Solvents. 4-Hydroxybenzaldehyde and 4-nitroacetophenone were recrystallized from distilled water and ethanol 95% respectively. 1,4-Diaminobenzene was sublimed at about 110 °C under vacuum (2−3 mm). Terephthaloyl chloride was recrystallized from n-hexane. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Benzaldehyde was purified by distillation under vacuum and a nitrogen atmosphere. Dimethylacetamide (DMAc) and dimethylformamide (DMF) were distilled over CaH_2. Toluene was distilled over Na. Triethylamine was dried by distillation over KOH. Thionyl chloride was purified by distillation. Analytical

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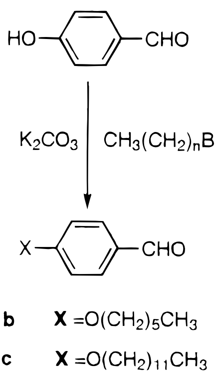
Scheme 1



grade 1,2-dichlorobenzene and 1-bromohexane and 1-bromododecane for synthesis were used without further purification. Hydrazine hydrate, boron trifluoride etherate, and acetic anhydride were used as supplied.

Preparation of Monomers. Preparation of Alkoxy-Substituted Benzaldehydes (Scheme 1). **4-(Hexyloxy)-benzaldehyde (1b).** A mixture of 4-hydroxybenzaldehyde (6.11 g, 50.00 mmol), 1-bromohexane (9.90 g, 60.00 mmol), potassium carbonate (7.60 g, 55.00 mmol), and DMF (50 mL) was refluxed overnight under N_2. The solvent and the excess of 1-bromohexane were removed by distillation. Water was added to the residue, and the product was extracted with ethyl acetate. The organic layer was dried with $MgSO_4$ and concentrated under vacuum to afford **1b** as a reddish liquid (9.50 g, 92%). It was used in the next step without further purification. IR (NaCl cells, cm^{-1}): 2932, 2860 (C−H stretching aliphatic); 1692 (CHO); 1602, 1578, 1510 (aromatic); 1468 (C−H bending aliphatic); 1258, 1160 (C−O−C). ^1H NMR, δ (ppm): 9.50 (s, 1H, CHO); 7.47, 7.43 (d, 2H, aromatic at positions 2 and 6); 6.60, 6.47 (d, 2H, aromatic at positions 3 and 5); 3.47 (t, 2H, $O-CH_2$); 0.88 (m, 8H, $-CH_2-$); 0.47 (t, 3H, $-CH_3$).

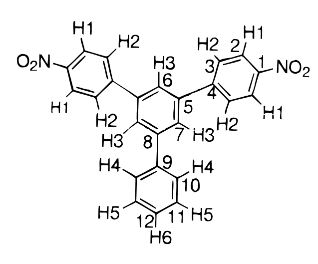
4-(Dodecyloxy)benzaldehyde (1c). It was prepared in 87% yield by reacting 1-bromododecane with 4-hydroxybenzaldehyde according to the procedure described for **1b**. IR (NaCl cells, cm^{-1}): 2924, 2854 (C−H stretching aliphatic); 1696 (CHO); 1602, 1578, 1510 (aromatic); 1466 (C−H bending aliphatic); 1258, 1160 (C−O−C). ^1H NMR, δ (ppm): 9.97 (s, 1H, CHO); 7.53, 7.48 (d, 2H, aromatic at positions 2 and 6); 6.67, 6.50 (d, 2H, aromatic at positions 3 and 5); 3.53 (t, 2H, $O-CH_2$); 0.90 (m, 20H, $-CH_2-$); 0.25 (t, 3H, $-CH_3$).

Preparation of Diamines 4 (Scheme 2). **2,6-Bis(4-nitrophenyl)-4-phenylpyrylium Tetrafluoroborate (2a).** Benzaldehyde (**1a**) (5.00 g, 47.12 mmol) and 4-nitroacetophenone (15.56 g, 94.23 mmol) were dissolved in toluene (30 mL) by slight heating. Boron trifluoride etherate (14.20 mL, 113.09 mmol) diluted with toluene (5 mL) was added dropwise to the stirred solution. The solution became red, and it was refluxed for 3 h under N_2. The dark solution obtained was concentrated under vacuum, and the residue was stirred with 1,4-dioxane at room temperature. The resulting green solid was filtered off, washed with 1,4-dioxane and then with ether, and dried to afford **2a** (13.51 g, 62%). Mp: 297−299 °C. IR (KBr, cm^{-1}): 1630, 1590, 1494 (aromatic and pyrylium structure); 1516, 1338 (NO_2); 1056 (br, BF_4^-). ^1H NMR (DMSO-d_6), δ (ppm): 8.87−7.93 (m, 4H, aromatic ortho to nitro groups and 2H, aromatic meta to O^+); 7.87−7.43 (m, 9H, other aromatic).

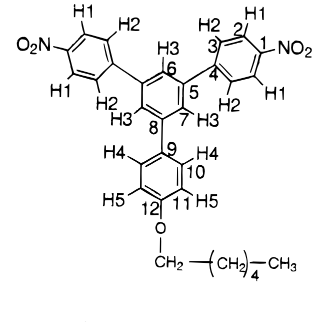
2,6-Bis(4-nitrophenyl)-4-[4-(hexyloxy)phenyl]pyrylium Tetrafluoroborate (2b). It was prepared in 61% yield as a brown-green solid by reacting **1b** with 4-nitroacetophenone according to the method applied for **2a**. It was recrystallized from acetic acid. Mp: 265−268 °C. IR (KBr, cm^{-1}): 2926, 2856 (C−H stretching aliphatic); 1634, 1584, 1492 (aromatic and pyrylium structure); 1524, 1348 (NO_2); 1248, 1188 (C−O−C); 1060 (br, BF_4^-). ^1H NMR (DMSO-d_6), δ (ppm): 8.71−7.93 (m, 4H aromatic ortho to nitro groups and 2H aromatic meta to O^+); 7.76−6.85 (m, 8H, other aromatic); 3.92 (t, 2H, $O-CH_2$); 1.60−1.21 (m, 8H, $-CH_2-$); 0.96 (t, 3H, $-CH_3$).

2,6-Bis(4-nitrophenyl)-4-[4-(dodecyloxy)phenyl]pyrylium Tetrafluoroborate (2c). **1c** (11.48 g, 39.59 mmol) and 4-nitroacetophenone (13.08 g, 79.18 mmol) were dissolved in 1,2-dichloroethane (35 mL) by slight heating. Boron trifluoride etherate (15.24 mL, 95.01 mmol) diluted with 1,2-dichloroethane (5 mL) was added dropwise. The solution was refluxed for 3 h under N_2 and then cooled at −10 °C overnight. The dark brown solid precipitate was filtered off, and washed with ether. It was subsequently stirred with ethyl acetate, filtered off and dried to afford **2c** as an orange-yellow solid (14.34 g, 54%). It was purified by recrystallization from acetic acid. Mp: 224−226 °C. IR (KBr, cm^{-1}): 2924, 2852 (C−H stretching aliphatic); 1636, 1584, 1492 (aromatic and pyrylium structure); 1526, 1350 (NO_2); 1250, 1188 (C−O−C); 1056 (br, BF_4^-). ^1H NMR (DMSO-d_6), δ (ppm): 8.86−7.94 (m, 4H aromatic ortho to nitro groups and 2H aromatic meta to O^+); 7.70−7.11 (m, 8H, other aromatic); 3.56 (t, 2H, $O-CH_2$); 1.66−0.97 (m, 20H, $-CH_2-$); 0.81 (t, 3H, $-CH_3$).

4,4″-Dinitro-5′-phenyl-*m*-terphenyl (3a). A mixture of **2a** (11.00 g, 23.51 mmol), fused CH_3COONa (3.86 g, 47.02 mmol), and acetic anhydride (40 mL) was refluxed overnight. The resulting solution was subsequently cooled at −10 °C for several hours, and the solid precipitate was filtered off, washed with methanol, and dried. Recrystallization from CH_2Cl_2 afforded **3a** as a light brown solid (6.71 g, 72%). Mp: 292−294 °C. IR (KBr, cm^{-1}): 1594 (aromatic); 1516, 1346 (NO_2). ^1H NMR (DMSO-d_6), δ (ppm): 8.35, 8.32 (d, 4H, H1); 8.23, 8.21 (d, 4H, H2); 8.13, 8.11 (d, 3H, H3); 7.93, 7.91 (d, 2H, H4); 7.55−7.43 (m, 3H, H5 and H6). ^{13}C NMR (DMSO-d_6), δ (ppm): 146.95 (C1); 146.10 (C4); 142.11 (C9); 139.45, 139.32 (C5 and C8); 128.91 (C11); 128.48 (C3); 128.02 (C10); 127.27 (C12); 126.24, 125.13 (C7 and C6); 123.92 (C2).

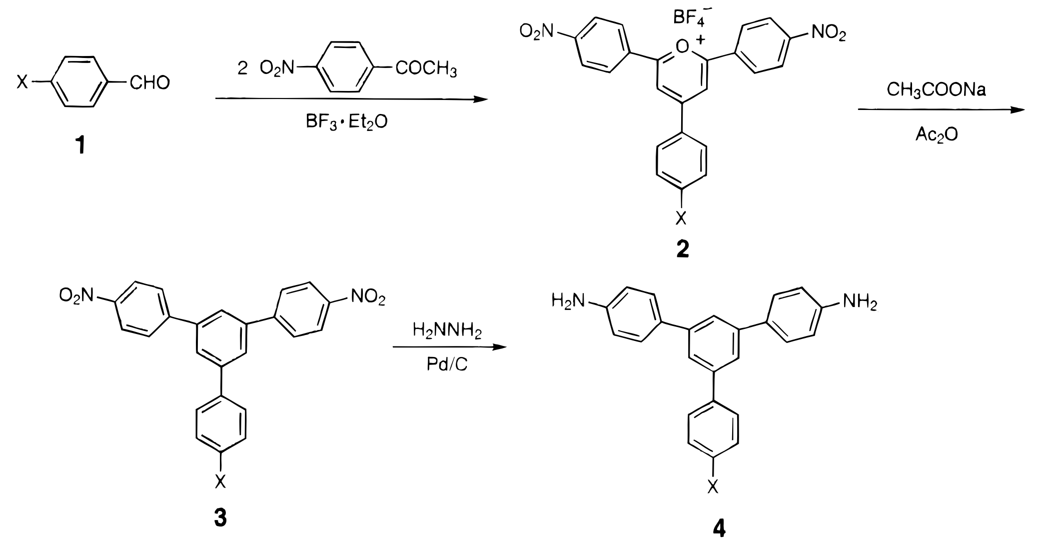


4,4″-Dinitro-5′-[4-(hexyloxy)phenyl]-*m*-terphenyl (3b). It was obtained in 61% yield as a light brown solid according to the procedure described for **3a** and recrystallized from nitromethane. Mp: 197−199 °C. IR (KBr, cm^{-1}): 2924, 2856 (C−H stretching aliphatic); 1594 (aromatic); 1514, 1344 (NO_2); 1252, 1182 (C−O−C). ^1H NMR (DMSO-d_6), δ (ppm): 8.35, 8.32 (d, 4H, H1); 8.25, 8.23 (d, 4H, H2); 8.18−7.85 (m, 5H, H3 and H4); 7.08, 7.06 (d, 2H, H5); 4.04 (t, 2H, $O-CH_2-$); 1.74−1.23 (m, 8H, $-CH_2-$); 0.87 (t, 3H, $-CH_3$). ^{13}C NMR (DMSO-d_6), δ (ppm): 158.28 (C12); 146.93, 146.25 (C1 and C4); 141.67 (C9); 139.43 (C5 and C8); 128.47 (C3); 125.68 (C7 and C6); 124.60 (C2); 123.92 (C10); 114.85 (C11); 67.55 ($O-CH_2$); 31.96, 28.61, 25.14, 22.03 ($(-CH_2-)_4$); 13.86 ($-CH_3$).



4,4″-Dinitro-5′-[4-(dodecyloxy)phenyl]-*m*-terphenyl (3c). It was obtained in 47% yield as a yellow-brown solid according to the procedure described for **3a** and was purified by recrystallization first from a mixture of 1,4-dioxane/nitromethane

Scheme 2

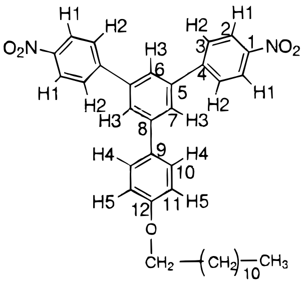


1a, 2a, 3a, 4a : X = H

1b, 2b, 3b, 4b : X = $O(CH_2)_5CH_3$

1c, 2c, 3c, 4c : X = $O(CH_2)_{11}CH_3$

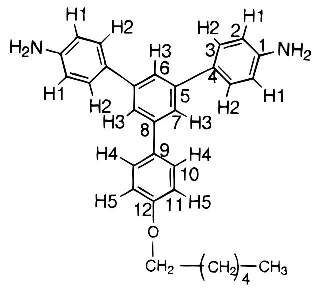
(2:1 v/v) and then from acetic acid. Mp: 166−168 °C. IR (KBr, cm^{-1}): 2920, 2850 (C−H stretching aliphatic); 1594 (aromatic); 1516, 1344 (NO_2); 1240, 1182 (C−O−C).



^{1}H NMR (DMSO-d_6), δ (ppm): 8.33, 8.31 (d,4H, H1); 8.17, 8.15 (d, 4H, H2); 8.03 (s, 3H, H3); 7.82, 7.80 (d, 2H, H4); 7.07, 7.05 (d, 2H, H5); 4.06 (t, 2H, −O−CH$_2$−); 1.76−1.28 (m, 20H, −CH$_2$−); 0.87 (t, 3H, −CH$_3$). ^{13}C NMR (DMSO-d_6), δ (ppm): 158.42 (C12); 147.42 (C1); 146.31 (C4); 141.98 (C8); 139.56 (C5); 131.70 (C9); 128.38, 128.31 (C3 and C10); 125.62 (C2); 124.49 (C6); 123.78 (C7); 115.18 (C11); 67.93 (−O−CH$_2$−); 31.14, 28.83, 28.68, 28.50, 25.41, 21.86 (−CH$_2$-)$_{10}$; 13.42 (−CH$_3$).

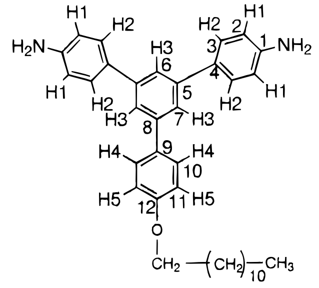
4,4″-Diamino-5′-phenyl-*m*-terphenyl (4a). A flask was charged with a mixture of **3a** (3.50 g, 8.33 mmol), ethanol 95% (10 mL) and a catalytic amount of palladium 10% on activated carbon. Hydrazine hydrade (4 mL), was added dropwise to the mixture at the boiling temperature, and refluxing was continued overnight. It was subsequently filtered, and **4a** was crystallized as a light brown solid upon cooling the filtrate at 0 °C (2.64 g, 89%). It was recrystallized from 1,2-dichlorobenzene. Mp: 206−207 °C. Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 84.59; H, 5.87; N, 8.24. IR (KBr, cm^{-1}): 3420, 3346 (N−H stretching); 1620 (N−H deformation); 1592, 1516 (aromatic); 1278 (C−N stretching). The ^{1}H NMR and ^{13}C NMR spectra are shown in Figure 1.

4,4″-Diamino-5′-[4-(hexyloxy)phenyl]-*m*-terphenyl (4b). It was prepared as a whitish solid in 95% yield according to the procedure described for **4a** and recrystallized from ethanol 95%. Mp: 150−152 °C. Anal. Calcd for $C_{30}H_{32}N_2O$: C, 82.53; H, 7.39; N, 6.42. Found: C, 81.48; H, 7.31; N, 6.46. IR (KBr, cm^{-1}): 3434, 3336 (N−H stretching); 2924, 2852 (C−H stretching aliphatic); 1610 (N−H deformation); 1594, 1514 (aromatic); 1282 (C−N stretching); 1258, 1182 (C−O−C).



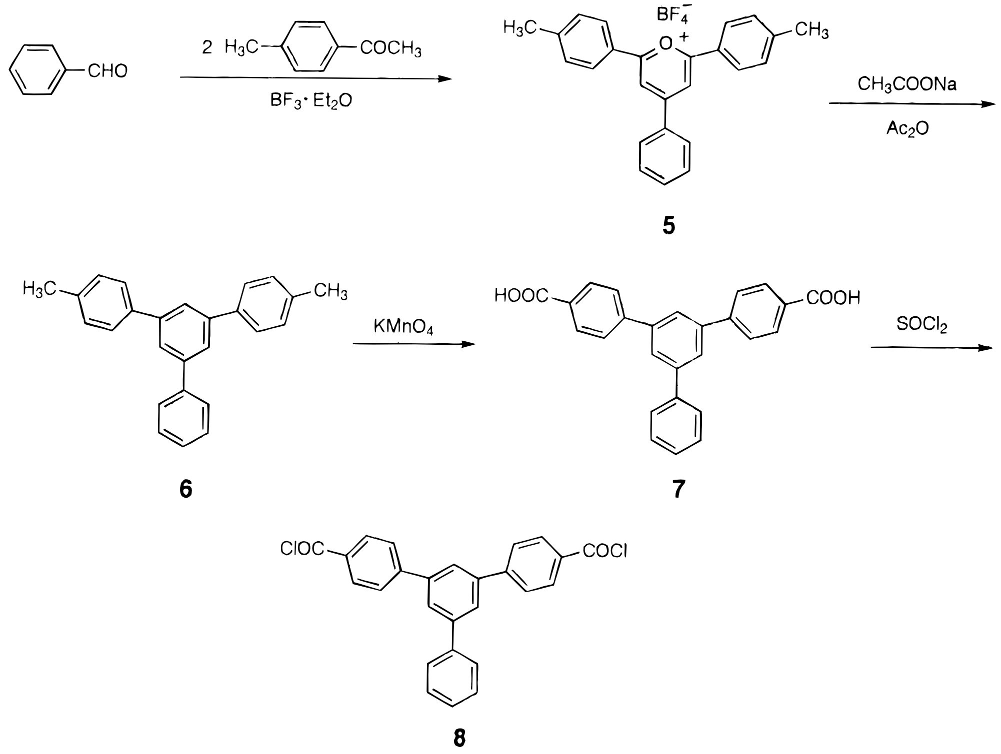
^{1}H NMR (DMSO-d_6), δ (ppm): 7.71−7.55 (m, 5H, H3 and H4); 7.50, 7.48 (d, 4H, H2); 7.03, 7.00 (d, 2H, H5); 6.68, 6.66 (d, 4H, H1); 5.21 (s, 4H, NH$_2$); 4.01 (t, 2H, O−CH$_2$); 1.75−1.31 (m, 8H, −CH$_2$−); 0.89 (t, 3H, −CH$_3$). ^{13}C NMR (DMSO-d_6), δ (ppm): 158.28 (C12); 148.40 (C1); 141.70, 140.75 (C5 and C8); 132.96 (C9); 127.97 (C4); 127.74 (C10); 127.44 (C3); 121.16, 120.99 (C6 and C7); 114.73 (C2); 114.13 (C11); 67.47 (O−CH$_2$−); 30.97, 28.64, 25.16, 22.03 (−CH$_2$-)$_4$; 13.86 (−CH$_3$).

4,4″-Diamino-5′-[4-(dodecyloxy)phenyl]-*m*-terphenyl (4c). It was prepared in 82% yield as a whitish solid as described for **4a** and was recrystallized from ethanol 75%. Mp: 129−130 °C. Anal. Calcd for $C_{36}H_{44}N_2O$: C, 83.03; H, 8.52; N, 5.38. Found: C, 82.32; H, 8.46; N, 5.27. IR (KBr, cm^{-1}): 3436, 3338 (N−H stretching); 2918, 2848 (C−H stretching aliphatic); 1610 (N−H deformation); 1596, 1514 (aromatic); 1282 (C−N stretching); 1250, 1182 (C−O−C).



^{1}H NMR (DMSO-d_6), δ (ppm): 7.70−7.55 (m, 5H, H3 and H4); 7.49, 7.47 (d, 4H, H2); 7.03, 7.00 (d, 2H, H5); 6.70, 6.68 (d, 4H, H1); 5.08 (s, 4H, NH$_2$); 4.03 (t, 3H, −O−CH$_2$−); 1.78−1.26 (m, 20H, −CH$_2$−); 0.86 (t, 3H, −CH$_3$). ^{13}C NMR (DMSO-

Scheme 3

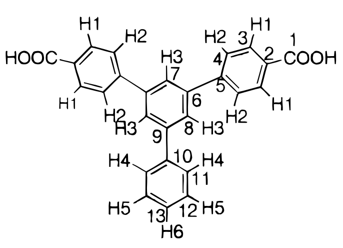


d_6), δ (ppm): 158.37 (C12); 148.31 (C1); 141.75, 140.81 (C5 and C8); 133.11 (C9); 128.01 (C4); 127.92 (C10); 127.38 (C3); 121.26, 121.08 (C6 and C7); 114.90 (C2); 114.27 (C11); 67.66 (−O−CH$_2$−); 54.68, 31.17, 28.85, 28.65, 28.55, 25.42, 21.94 (−CH$_2$-)$_{10}$; 13.75 (−CH$_3$).

Preparation of Dicarboxylic Acid Chloride 8 (Scheme 3**). 2,6-Bis(4-methylphenyl)-4-phenylpyrylium Tetrafluoroborate (5).** A flask was charged with a mixture of benzaldehyde (4.00 g, 37.69 mmol) and 4-methylacetophenone (10.18 g, 75.39 mmol). Boron trifluoride etherate (11.36 mL, 90.46 mmol) was added portionwise to the mixture at room temperature, and it was heated at 100 °C for 3 h. The resulting oil was diluted with ethyl acetate (8 mL). Ether (10 mL) was added to the solution, and it was cooled in a refrigerator. The yellow solid precipitate was filtered off, washed with ether, and dried to afford **5** (10.71 g, 67%). It was recrystallized from acetic acid. Mp: 264−266 °C. IR (KBr, cm^{-1}): 2916, 2860 (C−H stretching aliphatic); 1620, 1592, 1489 (aromatic and pyrylium structure); 1466 (C−H bending aliphatic); 1056 (br, BF$_4^-$). ^{1}H NMR (DMSO-d_6), δ (ppm): 8.86 (s, 2H, aromatic meta to O$^+$); 7.78−7.14 (m, 13H, other aromatic); 2.38 (s, 6H, CH$_3$).

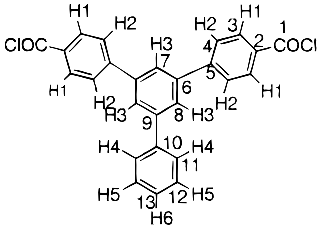
4,4″-Dimethyl-5′-phenyl-*m*-terphenyl (6). It was prepared as a yellowish solid in 61% yield according to the procedure described for **3a**. In some cases, methanol was added to the obtained solution before cooling. It was purified by recrystallization from a mixture of 95% ethanol/acetonitrile (3:1 v/v). Mp: 130−132 °C. IR (KBr, cm^{-1}): 2916, 2862 (C−H stretching aliphatic); 1596, 1514 (aromatic); 1466, 1392 (C−H bending aliphatic). ^{1}H NMR (DMSO-d_6), δ (ppm): 7.78 (s, 3H, aromatic at positions 2′, 4′, and 6′ of *m*-terphenyl); 7.64−7.05 (m, 13H, other aromatic); 2.35 (s, 6H, CH$_3$).

4,4″-Dicarboxy-5′-phenyl-*m*-terphenyl (7). A flask was charged with a solution of **6** (4.00 g, 11.98 mmol) in a mixture of pyridine (36 mL) and water (4 mL). After addition of potassium permanganate (5.30 g, 33.54 mmol), the solution was refluxed. Over a period of 8 h, potassium permanganate (10.79 g, 68.29 mmol) and water (25 mL) were added in portions to the refluxing solution. Refluxing was continued overnight. After cooling to room temperature, the mixture was filtered and the residual manganese dioxide was washed thoroughly with boiling water. The combined filtrates were acidified with hydrochloric acid. The white solid precipitate was filtered off, washed several times with water, and dried to afford **7** (3.87 g, 82%). It was recrystallized from a mixture of DMF/water (2:1 v/v). Mp: >300 °C. IR (KBr, cm^{-1}): 3069−2548 (O−H stretching); 1688 (C=O); 1608, 1574, 1510 (aromatic); 1422, 1288 (C−O stretching and O−H deformation).

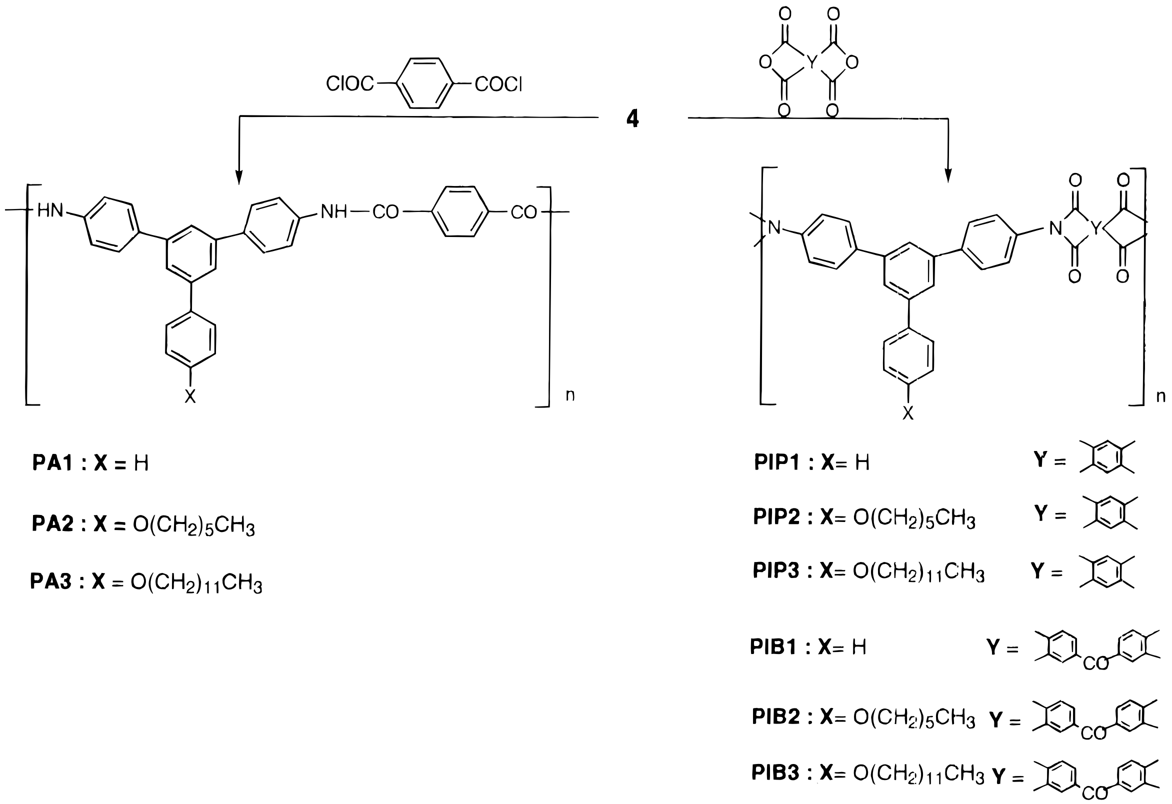


^{1}H NMR (DMSO-d_6), δ (ppm): 13.17 (br, 2H, COOH); 8.04−7.95 (m, 8H, H1 and H2); 7.87 (s, 3H, H3); 7.60−7.41 (m, 5H, H4, H5 and H6). ^{13}C NMR (DMSO-d_6), δ (ppm): 166.62 (C1); 143.98 (C5); 141.88 (C6 and C9); 140.58 (C10); 132,74 (C3); 129.86 (C2); 129.37, 128.88, 127.81, 127.29 (C4, C11, C12 and C13); 125.29 (C7 and C8).

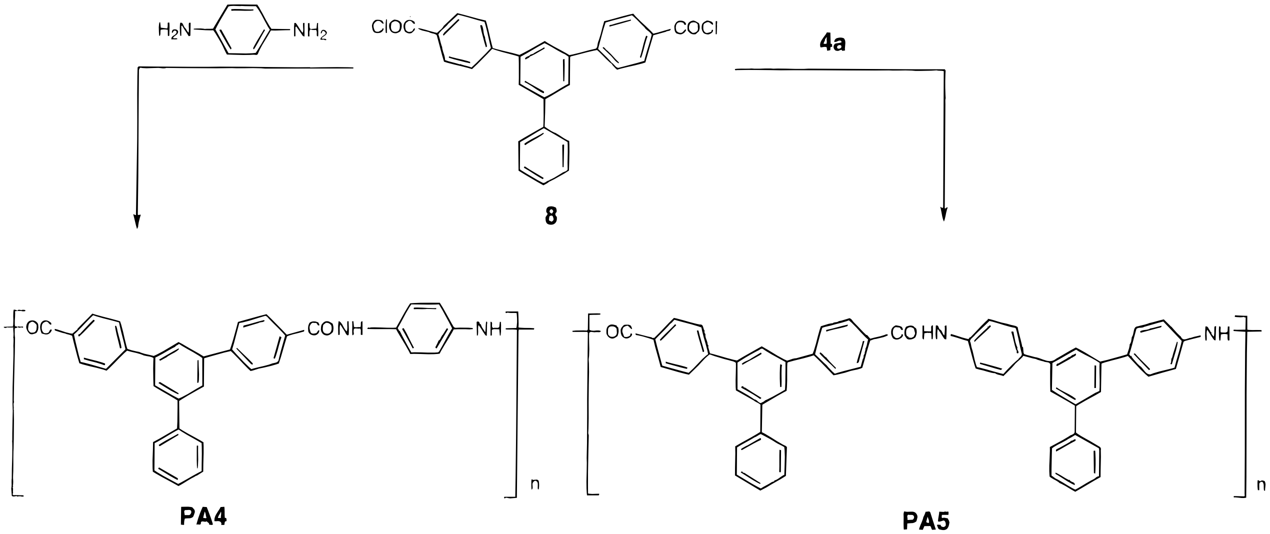
4,4″-Bis(chlorocarbonyl)-5′-phenyl-*m*-terphenyl (8). A mixture of **7** (2.50 g, 6.35 mmol), thionyl chloride (15 mL), and DMF (1 mL) was refluxed overnight. The solution obtained was concentrated under vacuum, and the residue was stirred with ether, filtered off, washed with ether, and dried to afford **8** as a whitish solid (2.03 g, 74%). It was recrystallized from chloroform. Mp: 191−193 °C. Anal. Calcd for $C_{26}H_{16}O_2Cl_2$: C, 72.40; H, 3.74. Found: C, 71.54; H, 3.68. IR (KBr, cm^{-1}): 1768, 1738 (C=O); 1598 (aromatic); 1208, 1178 (−C−C=O stretching).



Scheme 4



Scheme 5



^{1}H NMR (CDCl$_3$ at 55 °C), δ (ppm): 8.24, 8.22 (d, 4H, H1); 7.87−7.81 (m, 7H, H2 and H3); 7.68, 7.66 (d, 2H, H4); 7.52−7.48 (m, 3H, H5 and H6). ^{13}C NMR (CDCl$_3$ at 55 °C), δ (ppm): 166.01 (C1); 147.49 (C5); 143.38 (C10); 140.81 (C9); 140.24 (C6); 132.68 (C2); 132.00 (C3); 129.02 (C12); 128.10 (C4); 127.75 (C11); 127.29 (C13); 126.63 (C7); 125.51 (C8).

Preparation of Polymers (Schemes 4 and 5). As a typical example the preparation of polyamide **PA1** is given.

A flask was charged with a solution of **4a** (1.35 g, 4.01 mmol) in DMAc (30 mL). Triethylamine (0.81 g, 8.02 mmol) was added to the solution, and it was cooled at −10 °C. Terephthaloyl chloride (0.81 g, 4.01 mmol) dissolved in DMAc (12 mL) was added to the stirred solution at −10 °C under N$_2$. Stirring under N$_2$ was continued at this temperature for 5 h and then at room temperature overnight. The solution was poured into water, and the pale brown solid precipitate was filtered off, washed with water and then with hot acetone, and dried (1.81 g, 97%).

The preparation of polyimide **PIP1** is given as a general procedure for the synthesis of polyimides.

PMDA (0.65 g, 2.97 mmol) was added to a stirred solution of **4** (1.00 g, 2.97 mmol) in DMAc (20 mL) at 0 °C. The solution became viscous and diluted with DMAc (20 mL). Stirring was continued for 5 h under N$_2$. The solution was subsequently heated at about 100 °C, and acetic anhydride (5 mL) and pyridine (2 mL) were added. Heating was continued at this temperature overnight. The solution was poured into water and the brown solid precipitate was filtered off, washed with water and then with hot acetone and dried (1.50 g, 97%).

The reaction yields, the inherent viscosities, and the elemental analyses of all polymers are given in Table 1.

Results and Discussion

Three new aromatic diamines of *m*-terphenyl were synthesized according to the reaction sequence of Scheme

Table 1. Reaction Yields, Inherent Viscosities, and Elemental Analyses of Polymers

polymer	yield (%)	n_{inh} (dL/g)	empirical formula		elemental analyses (%)		
					C	H	N
PA1	97	1.12[a]	$(C_{32}H_{22}N_2O_2)_n$	calcd	82.38	4.75	6.00
				found	81.12	4.63	5.87
PIP1	97	1.37[b]	$(C_{34}H_{18}N_2O_4)_n$	calcd	78.76	3.50	5.40
				found	78.14	3.42	5.28
PIB1	93	1.23[b]	$(C_{41}H_{22}N_2O_5)_n$	calcd	79.09	3.56	4.50
				found	78.32	3.48	4.56
PA2	99	1.31[a]	$(C_{38}H_{34}N_2O_3)_n$	calcd	80.54	6.05	4.94
				found	79.47	5.92	4.91
PIP2	96	1.46[b]	$(C_{40}H_{30}N_2O_5)_n$	calcd	77.65	4.89	4.53
				found	76.49	4.98	4.59
PIB2	100	1.39[b]	$(C_{47}H_{34}N_2O_6)_n$	calcd	78.10	4.74	3.88
				found	77.65	4.79	3.83
PA3	94	0.76[a]	$(C_{44}H_{46}N_2O_3)_n$	calcd	81.20	7.12	4.30
				found	80.46	7.03	4.24
PIP3	98	1.14[b]	$(C_{46}H_{42}N_2O_5)_n$	calcd	78.61	6.02	3.99
				found	77.53	6.10	3.86
PIB3	89	0.98[b]	$(C_{53}H_{46}N_2O_6)_n$	calcd	71.16	7.85	4.74
				found	70.25	7.76	4.68
PA4	90	0.92[a]	$(C_{32}H_{22}N_2O_2)_n$	calcd	82.38	4.75	6.00
				found	81.21	4.63	5.87
PA5	95	0.51[c,d]	$(C_{50}H_{34}N_2O_2)_n$	calcd	86.43	4.93	4.03
				found	85.84	4.87	3.92

[a] Inherent viscosity in DMAc (0.5 g/dL) at 30 °C. [b] Inherent viscosityof intermediate poly(amic acids) in DMAc (0.5 g/dL) at 30 °C. [c] Inherent viscosity in H_2SO_4 (0.5 g/dL) at 30 °C. [d] Precipitation during polymerization.

2. Benzaldehyde or 4-alkoxy-substituted benzaldehydes, prepared as shown in Scheme 1, were used as starting materials. They reacted with 4-nitroacetophenone in the presence of $BF_3{\cdot}Et_2O$ to yield the pyrylium salts **2**. The latter reacted with acetic anhydride/sodium acetate, leading to the substituted dinitro-*m*-terphenyls **3**. It is well established that 2,4,6-triarylpyrylium salts react with excess carboxylic acid anhydrides in the presence of a condensing agent like sodium acetate, affording 1,3,5-triarylbenzene.[35,36] Compounds **3** were catalytically hydrogenated to the corresponding diamines **4** by means of hydrazine hydride.

In addition, the substituted dicarboxy-*m*-terphenyl **7** and the corresponding acid chloride **8** were similarly prepared starting from benzaldehyde and 4-methylacetophenone (Scheme 3). The intermediate dimethyl compound was oxidized using $KMnO_4$.

The structures of monomers were confirmed by elemental analyses as well as IR and NMR spectroscopy. Figure 1 presents typical ^1H NMR and ^{13}C NMR spectra of diamine **4a** in DMSO-d_6 solution. Assignments of peaks for both spectra are given in the figure. In the ^1H NMR spectrum the amino protons were exchangeable with D_2O. The aromatic protons ortho to NH_2 groups were clearly distinguished, whereas the other aromatic protons were partially overlapped. All carbon nuclei gave well-separated peaks in the ^{13}C NMR spectrum.

Certain structural characteristics of diamine **4a** were estimated using a modeling system. The optimized geometry of this diamine as calculated by means of CS Chem3D Pro v. 3.2 modeling system indicated that the structure deviates significantly from the coplanar conformation, since two adjacent phenyl rings form a dihedral angle of about 45°. Such a twist is greater than that (~23°) observed between two adjacent phenyls in nonsubstituted polyphenylenes.[37]

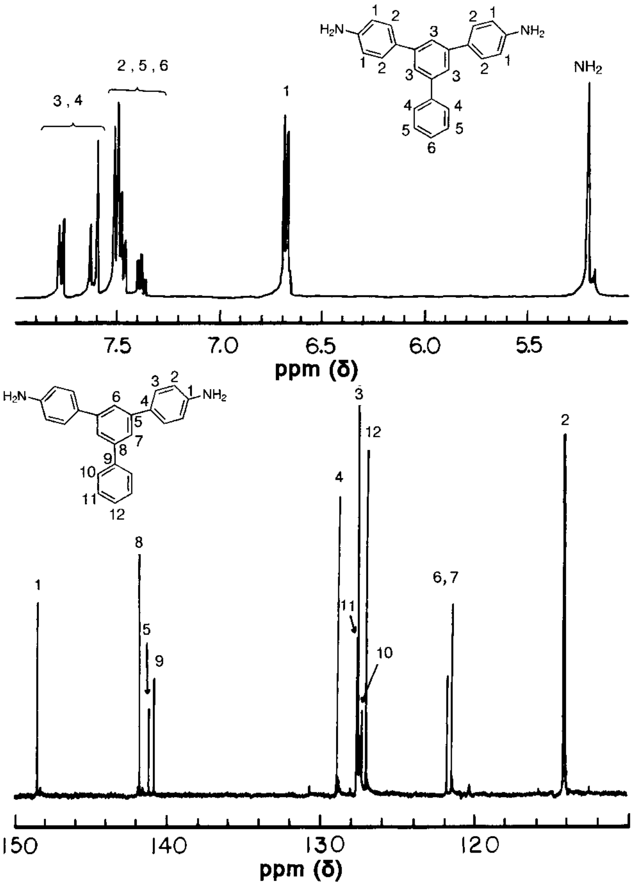


Figure 1. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of compound **4a** in DMSO-d_6 solution.

Diamines **4** reacted with terephthaloyl chloride or tetracarboxylic dianhydrides (PMDA and BTDA) to afford polyamides **PA** and polyimides **PIP** and **PIB**, respectively (Scheme 4). In addition, dicarboxylic acid chloride **8** reacted with 1,4-diaminobenzene or diamine **4a** to yield polyamides **PA4** and **PA5**, respectively (Scheme 5).

The polymers were obtained in 89−100% yields and their inherent viscosities ranged from 0.51 to 1.46 dL/g. Since polyimides were partially soluble in polar aprotic solvents, the n_{inh} of the intermediate poly(amic acids) were determined by taking an aliquot from their solutions in DMAc and diluting before making the measurements.

Structural characterization of polymers was accomplished by elemental analyses, IR, NMR, and UV−vis spectroscopy as well as X-ray. Figure 2 presents the FT-IR spectra of polyamides **PA1** and **PA4**. Since they had comparable structures, they displayed the same pattern with characteristic absorptions around 3300 (N−H stretching), 1650 (C=O), 1600 (N−H deformation), and 1312 cm^{-1} (C−N stretching and N−H bending). Figure 3 shows a typical FT-IR spectrum of **PIP1**, which exhibited absorptions at 1778, 1724, 1364, and 1088 cm^{-1} associated with the imide structure. As polyimides **PIP**, derived from PMDA, and **PIB1** were insoluble even in polar aprotic solvents, their structures were verified by IR spectroscopy.

Figures 4 and 5 present the ^1H NMR and ^{13}C NMR spectra, respectively, of polyamide **PA2**. Both spectra are in agreement with the proposed structure. Peak assignments are given in the figures.

The absorption spectra of three typical polyamides were obtained from DMF solution and correlated with their structures. Specifically, the UV−vis absorption

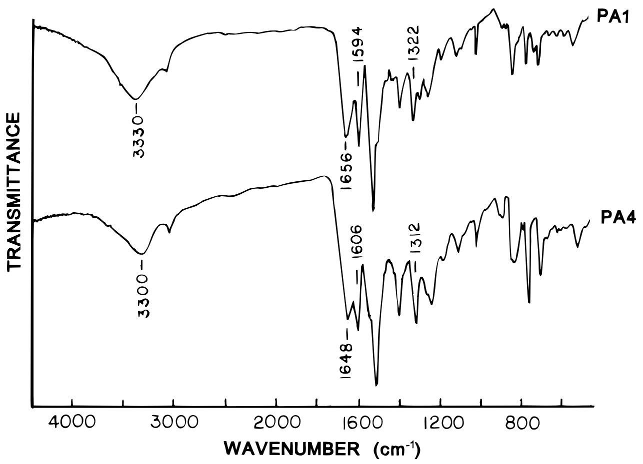


Figure 2. FT-IR spectra of polyamides **PA1** and **PA4**.

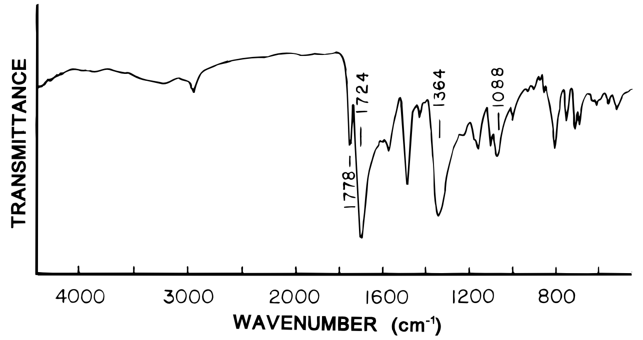


Figure 3. FT-IR spectrum of polyimide **PIP1**.

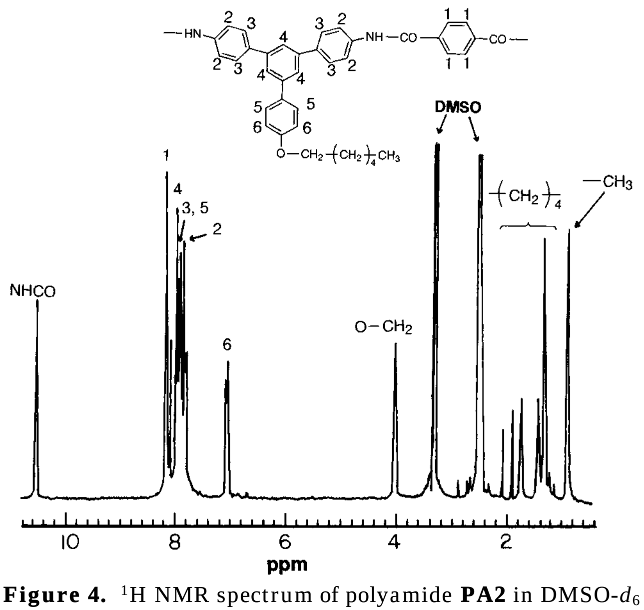


Figure 4. ^{1}H NMR spectrum of polyamide **PA2** in DMSO-d_6 solution.

spectra of polyamides **PA1**, **PA2**, and **PA4** showed maxima at 313, 328, and 314 nm, respectively. Their absorption curves were not extended into the visible region. This feature was attributed to the presence of meta linkages that interrupt a long-range conjugation.[35] The identical absorption maxima of **PA1** and **PA4** support that they had the same electronic properties in solution, regardless of the incorporation of *m*-terphenyls in the diamine or dicarboxylic acid segment. The introduction of the electron-donating hexyloxy groups altered the electron structure of **PA2**, and the maximum was shifted to the longer wavelength. This conforms with literature data concerning poly(*m*-phenylenes)[38] and poly(*p*-phenylenes).[39]

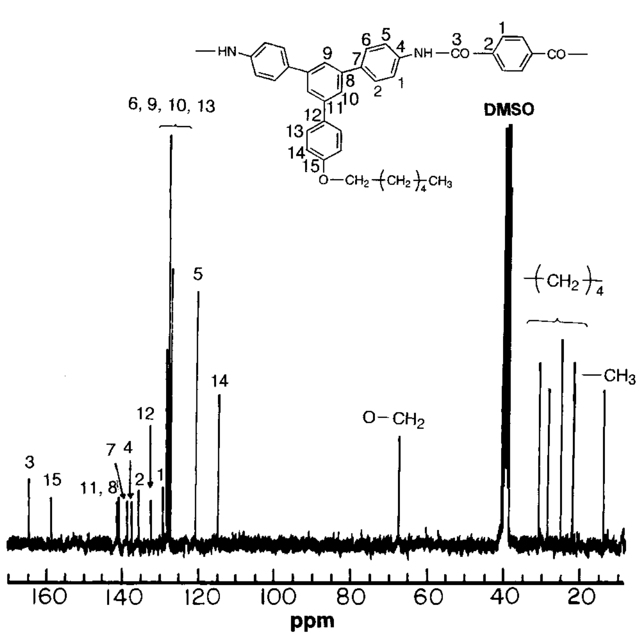


Figure 5. ^{13}C NMR spectrum of polyamide **PA2** in DMSO-d_6 solution.

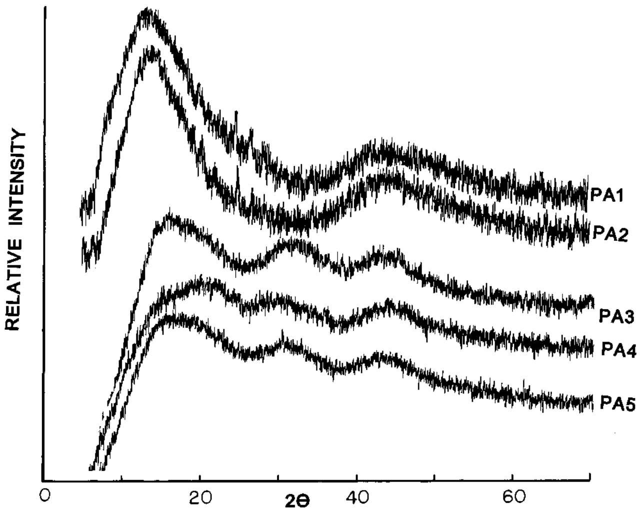


Figure 6. X-ray diffraction patterns of polyamides.

An attempt was made to estimate the crystallinity of polymers by means of X-ray diffractograms. Figure 6 presents the wide-angle X-ray diffractograms of the synthesized polyamides obtained with as prepared powders. Generally, both polyamides and polyimides displayed amorphous nature. It seems that polyamides **PA1** and **PA2** showed nearly identical patterns. When these polyamides are compared with the other three, it seems that the former displayed a strong reflection hump approximately between $2\theta = 7$ and 25°, indicating a higher packing density.[40] Since these peaks had the same intensity and broadness, the incorporation of the pendent hexyloxy groups along the polymer backbone in **PA2** did not significantly affect the chain packing. In contrast, the presence of the pendent dodecyloxy groups in **PA3** remarkably changed the diffraction pattern and increased the disorder in chains.

One objective of the present investigation was the preparation of processable soluble polyamides and polyimides. For this aim, the *m*-terphenyl segments were

Table 2. Solubilities of Polyamides[a]

	solvents[b]								
polyamide	DMF	NMP	DMSO	CCl_3COOH	H_2SO_4	1,4-dioxane	CH	DCB	TCE
PA1	++	++	++	+−	+	−	+−	−	−
PA2	++	++	++	+	+	−	++	−	+−[c]
PA3	++	++	++	+	+	+	++	+[c]	+[c]
PA4	++	++	++	+	++	+−	+−	−	−
PA5	+−	+−	+−	+−	+	−	+−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +-, partially soluble, − insoluble. [b] DMF, *N*,*N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide; CH, cyclohexanone; DCB, 1,2-dichlorobenzene; TCE, 1,1,2,2-tetrachloroethane. [c] Gel is formed on cooling.

Table 3. Solubilities of Polyimides[a]

	solvents[b]								
polyimide	DMF	NMP	DMSO	CCl_3COOH	H_2SO_4	1,4-dioxane	CH	DCB	TCE
PIP1	+−	+−	+−	+−	+	−	−	−	−
PIB1	+−	+−	+−	+−	+	−	−	−	−
PIP2	+−	+−	+−	+−	+	−	−	−	−
PIB2	+	+	+	+	+	+−	−	−	−
PIP3	+−	+−	+−	+−	+	−	−	−	−
PIB3	+	+	+	+	+	+	+	−	−

incorporated in the main chain, which should be more soluble than p-terphenyls. In addition, phenyl or 4-alkoxyphenyl pendent groups were introduced at the 5′ position of *m*-terphenyls in order to increase further the polymer solubility. Tables 2 and 3 outline the solubilities of polyamides and polyimides, respectively. Polyamide **PA1** was readily soluble in polar aprotic solvents (DMF, NMP, DMSO) at room temperature and H_2SO_4 upon heating. Polyamide **PA2** possessing 4-(hexyloxy)-phenyl pendent groups showed a slightly higher solubility, being soluble moreover in cyclohexanone and CCl_3COOH. Increasing the side aliphatic chain to dodecyloxy the solubility was remarkably enhanced. Thus, polyamide **PA3** was soluble in all tested solvents even in less efficient ones such as 1,4-dioxane, 1,2-dichlorobenzene, and 1,1,2,2-tetrachloroethane. The enhanced solubility of **PA3** reflects to the less chain packing of this polymer, which was detected by X-ray (see above). Polyamide **PA4** displayed a comparable solubility with **PA1**, thus supporting that the presence of *m*-terphenyl in either diamine or dicarboxylic acid moiety did not affect noticeably the polymer solubility. Finally, polyamide **PA5** showed poor solubility owing to the increased rigidity.

It is seen from Table 3 that the polyimides **PIP1**, **PIP2**, and **PIP3** derived from PMDA were soluble only in warm H_2SO_4. This behavior suggests that the presence of the pendent groups did not influence the polymer solubility. However, in the case of polyimides prepared from BTDA the side chain improved their solubility, which followed the trend of polyamides.

When solutions of polymers in DMF or concentrated H_2SO_4 were examined under polarized microscopy, they did not display lyotropic behavior. Taking into consideration that some of the our previously synthesized polyamides containing p-terphenyl units[31] exhibited lyotropic behavior, the absence of lyotropism of the present polyamides could be attributed to the meta linkages that reduced the chain stiffness.

The hydrophilicity of polyamides **PA1**, **PA2**, **PA3**, **PA4**, and **PA5** was estimated by determination of their isothermal water absorption. After an exposure time of 50 h, the water uptake was 1.31, 1.26, 2.45, 6.09, and 6.84%, respectively. The corresponding numbers of moles of absorbed water per amide equivalent weight were 0.17, 0.20, 0.44, 0.79, and 1.32. The higher chain packing, detected by the X-ray method, of polyamides **PA1** and **PA2** reduced the water accessibility, thereby their hydrophilicity.

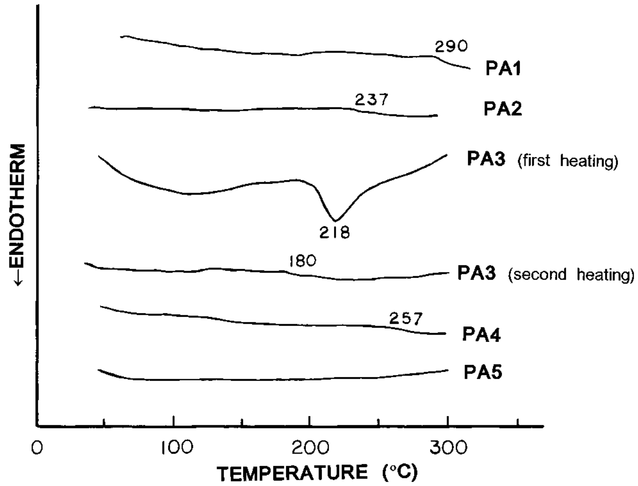


Figure 7. DSC thermograms of polyamides **PA1**, **PA2**, **PA4**, and **PA5** (second heating) as well as of polyamide **PA3** (first and second heating). Conditions: N_2 flow 60 cm^3/min; heating rate 20 °C/min.

Interestingly, **PA4** showed considerably higher hydrophilicity than **PA1**. The only structural difference between these polyamides is the orientation of the amide groups. An attempt was made to estimate the deviation from plane of two model diamides by means of CS Chem3D modeling system. More particularly, the model diamide of **PA1** had a factor of deviation from plane (FDP) of 0.62, while the model diamide of **PA4** had FDP 1.00. Note that for a completely coplanar structure the value of FDP is zero. The results suggest that **PA4** possesses a more twisted structure than **PA1**, which leads to a less chain packing, thus allowing higher water accessibility.

Thermal characterization of polymers was accomplished by DSC and TMA. Figure 7 depicts the DSC traces of the synthesized polyamides in a N_2 atmosphere. Polyamides **PA1**, **PA2**, **PA3**, and **PA4** displayed T_g's at 290, 237, 180, and 257 °C, respectively. No T_g transition was detected for polyamide **PA5**. It is obvious that the presence of the alkoxy pendent groups

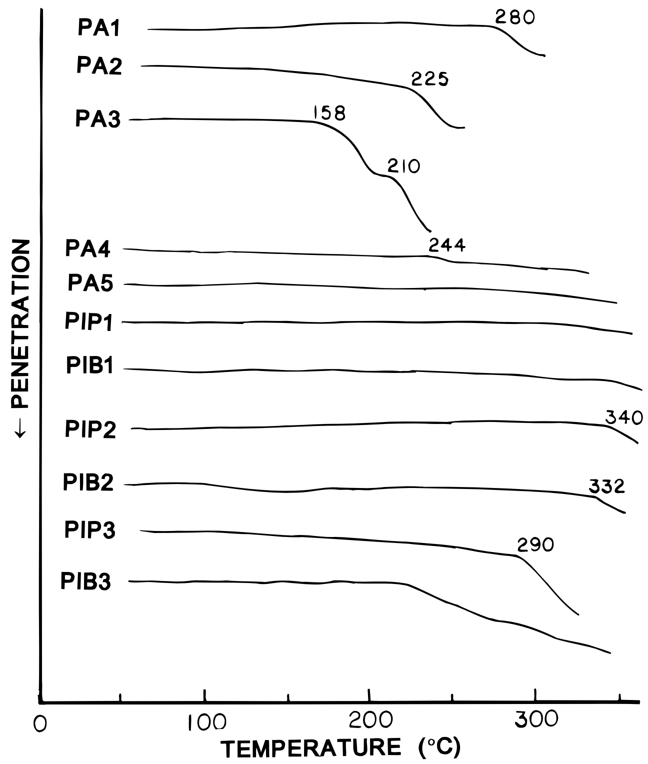


Figure 8. TMA traces of polymers. Conditions: N_2 flow 60 cm^3/min; heating rate 20 °C/min.

Table 4. Thermal Stabilities of Polymers

	In N_2				In Air			
polymer	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)	wt loss[e] (%)
PA1	385	493	517	70	351	467	487	8.2
PIP1	404	578	619	75	392	501	519	3.8
PIB1	426	582	671	80	411	537	563	1.3
PA2	355	530	571	66	325	430	467	11.3
PIP2	385	489	600	68	380	484	489	7.6
PIB2	397	510	589	78	392	498	517	6.1
PA3	347	448	471	47	310	411	433	14.9
PIP3	380	552	616	62	375	471	527	13.7
PIB3	389	478	478	66	385	486	456	11.7
PA4	377	493	552	64	367	464	489	8.7
PA5	397	517	533	71	377	482	527	5.3

[a] Initial decomposition temperature. [b] Polymer decomposition temperature. [c] Maximum polymer decomposition temperature. [d] Char yield at 800 °C. [e] Weight loss after 20 h isothermal aging at 300 °C in static air.

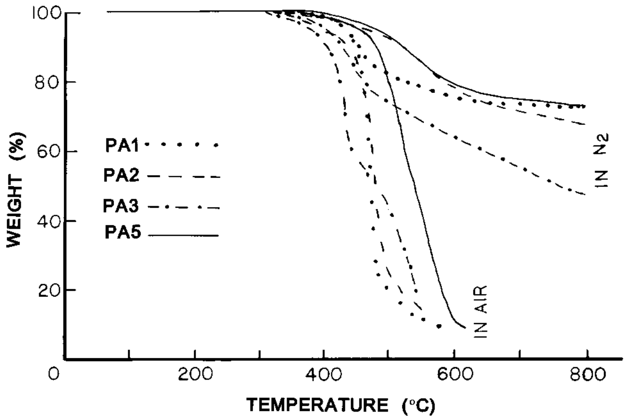


Figure 9. TGA thermograms in N_2 and air of polyamides **PA1**, **PA2**, **PA3**, and **PA5**. Conditions: Gas flow 60 cm^3/min; heating rate 20 °C/min.

reduced the T_g's and the reduction was greater for the longer aliphatic side group. The long alkyl chains along the polymer backbone increase the polymer's free volume, thus resulting in a reduction in the T_g. The lower T_g of **PA4** than of **PA1** suggests that the attachment of the *m*-terphenyl in the dicarboxylic acid moiety reduced the chain rigidity. Furthermore, an endotherm associated with softening was observed at 218 °C during the first heating of polyamide **PA3** bearing the dodecyloxy pendent groups. Such a behavior could be attributed to the gain in entropy that is brought about from the vast number of conformations of dodecyloxy groups in the melt.[20] No distinct transitions were detected by DSC up to 300 °C for all polyimides.

The T_g and T_s of polymers were also determined by TMA (Figure 8). The T_g's of polyamides determined by TMA were 10−22 °C lower than those of DSC. In the case of **PA3**, the relaxation at 210 °C was assigned to softening. No T_g was detected up to 350 °C for **PA5**, which contains two *m*-terphenyls per repeat unit. This feature reveals the increased rigidity of **PA5** versus the other polyamides synthesized and conforms with its poorer solubility. Polyimides **PIP1** and **PIB1** without alkoxy pendent groups did not show a T_g up to 350 °C. In contrast, **PIP2** and **PIB2** containing hexyloxy groups showed T_g's at high temperatures, 340 and 332 °C, respectively. Polyimide **PIP3** with dodecyloxy side groups displayed T_g at 290 °C, whereas no T_g was determined for **PIB3** due to a gradual relaxation that began at approximately 220 °C.

The thermal stability of polymers was ascertained by TGA and isothermal gravimetric analysis (IGA). The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}) in both N_2 and air, and the anaerobic char yield (Y_c) at 800 °C for all polymers are summarized in Table 4. The IDT and PDT were determined for the temperature at which 0.5 and 10% weight loss were observed, respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred. Figure 9 presents typical TGA traces of polyamides **PA1**, **PA2**, **PA3**, and **PA5** in N_2 and air. The polymers without alkoxy groups were more thermally stable than the corresponding ones with alkoxy substituents. It seems that when the length of the aliphatic group increased, the thermal stability of the polymers was reduced. Polyamide **PA5** containing two *m*-terphenyl segments per repeat unit was the most thermally stable among the polyamides synthesized.

Conclusions

A convenient method utilizing pyrylium salts was applied for the synthesis of three new diamines and one dicarboxylic acid of phenyl- or 4-alkoxyphenyl-substituted *m*-terphenyl. Rigid-rod polyamides and polyimides were prepared from them. X-ray studies showed that all polymers were amorphous and that the polyamides **PA1** and **PA2** had higher chain packings than the other. The polyamides containing one *m*-terphenyl segment per repeat unit were soluble in polar aprotic solvents. The solubility of polyamides as well as of polyimides derived from BTDA was remarkably increased by incorporating 4-(hexyloxy)phenyl and especially 4-(dodecyloxy)phenyl as pendent groups along the polymer backbone. Only polyamide **PA3** bearing 4-(dodecyloxy)phenyl side groups showed softening. The presence of the alkoxy substituents reduced the T_g of all polymers, and the reduction was greater for the dodecyloxy group. Wholly aromatic polyamides and polyimides displayed an excellent thermal stability.

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